INFLUENCE OF MOLECULAR WEIGHT ON THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF POLYSTYRENE*

A. I. MAKLAKOV and E. I. NAGUMANOVA

Kazan State University

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THE nuclear magnetic resonance (NMR) spectra of polymers are usually recorded for polydisperse specimens, for which reason the effect of their molecular weight (M) has still not been finally ascertained. In [1] four specimens of atactic polystyrene (PS) were studied with $M=1{\cdot}25\times10^5$, $1{\cdot}6\times10^5$, $2{\cdot}67\times10^5$ and $3{\cdot}5\times$ $\times10^6$, and the size of the molecule was not found to have any effect on the NMR spectra. But in a study of fractionated PS specimens with $M=1{\cdot}5\times10^6$ and $4{\cdot}47\times$ $\times10^5$ in [2], the sudden contraction of the NMR line was found to occur at a rather higher temperature for the first than for the second specimen. A different effect was found on the example of polytrifluorochloroethylene in [3], and the authors attributed it to the fact that the crystallization of the specimen was dependent on the macromolecular size.

We have made an attempt to studying the influence of molecular weight on the NMR spectra of fractionated atactic PS with the M of the fractions varying in a wide range between $1{\cdot}8\times10^3$ and $1{\cdot}25\times10^6$. The present work deals with the results.

EXPERIMENTAL PROCEDURE

Fractional precipitation was used, with the addition of an agent [4]. Benzene was the solvent used, and methanol the precipitating agent [5]. The fractionation was from 1% (for high-molecular weight) and 3% solutions (for low-molecular weight fractions). The high-molecular weight fractions were prepared from commercial bulk PS with viscosity-average $M=3{\cdot}6\times10^5$, and granulated PS with $M=7{\cdot}6\times10^5$. To produce the low-molecular fractions in sufficient quantity (~1 g) low-molecular weight bulk PS was specially synthesized. The polymerization was conducted at 100 and 135° for 90 min with the addition of 3% benzoyl peroxide as initiator. The viscosity-average molecular weights of the polymers produced in this way were $\sim2\times10^4$ and 1×10^4.

The molecular weights of the fractions produced were determined viscometrically in benzene solutions [4]. Nine PS fractions were produced and studied, with molecular weights $1{\cdot}8\times10^3$, 5×10^3, 7×10^3, 1×10^4, $1{\cdot}32\times10^4$, $3{\cdot}05\times10^4$, 7×10^4, $5{\cdot}6\times10^5$, $1{\cdot}25\times10^6$. The fractions with $M=1\times10^4$, $3{\cdot}05\times10^4$ and $7{\cdot}10^4$ were prepared twice from different batches of PS, which showed that the shape of their spectra did not depend on the method of production.

Residues of solvent and precipitator were removed from the specimens by vacuum treatment at 10^{-2} mmHg and 60° for 3 hr.

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